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Reactive Ion Etching of SiC Thin Films by Mixtures of Fluorinated Gases and Oxygen

by

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REACTIVE ION ETCHING OF SiC THIN FILMS BY MIXTURES OF FLUORINATED GASES AND OXYGEN

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ABSTRACT

Reactive ion etching (RIE) of SiC thin films has been investigated in depth in a variety of fluorinated gas plasmas, such as SF_6, $CBrF_3$ and CHF_3 mixed with oxygen. The optical emission spectrum of the RF plasma and the plasma-induced DC bias were monitored to explore the etching mechanisms. Argon actinometry has been used to convert the plasma emission intensity to relative concentration of plasma species in order to more accurately quantify the etching process. Plasma conditions, such as composition of gas mixture, pressure, power were investigated in order to achieve selective SiC-to-Si etching

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and anisotropic patterning of SiC thin films. A SiC:Si etch rate ratio higher than unity was obtained for the first time by using $CBrF_3/75\%O_2$ and $CHF_3/90\%O_2$ at 200W, 20sccm, 20mTorr plasma conditions. The best anisotropic profile was obtained by using CHF_3 gas in the RIE mode. A critical DC bias level, around -300V, appears to separate regimes of chemical and physical rate-limiting step domination of the SiC etch rate. A carbon-rich surface on the etched SiC films was found for all gases. The SiC etching mechanisms in fluorinated gases was deduced from loading experiments, surface analysis and other etching phenomena. Evidence of the chemical reaction between carbon and oxygen is presented. No evidence of chemical reaction between fluorine and carbon has been observed. A combined chemical and physical etching model, supported by experiments, is suggested. A carbon blocking mechanism is proposed to understand the etching profile in all etching gases.

1. INTRODUCTION

As device fabrication technology pushes deeper into the submicron region, and therefore towards ever higher device density, the requirements for devices working under conditions of higher heat dissipation, higher operating temperature and higher electrical field have become more difficult to meet by conventional semiconductor materials, such as Si and GaAs, because of their basic material properties. Silicon carbide (SiC) is a semiconductor which enjoys a number of superior properties which can be of great potential benefit when developed in conjunction with advances in submicron semiconductor processing technology. SiC has become an attractive semiconductor material in recent years for high speed, high density and high temperature device applications due to its wide band gap [1], high thermal conductivity, high temperature stability, high breakdown electric field [2] and high electron saturation velocity [3,4]. In this work we have used the sputtering technique to prepare SiC thin films. This has the advantage of being essentially

substrate-independent, taking place at close to room temperature and being able to cover large areas fairly easily. Currently, the major applications of SiC devices are in solar cells [5], light-emitting devices [6], and SiC-Si heterojunction devices [7,8].

The use of plasma etching to pattern SiC thin films has been investigated for a number of gases: Ar [9], CF_4 [10,11], CF_4/O_2 [9, 11, 12], NF_3 [13], SF_6 [14], SF_6/He [9]. These previous reports mainly concentrated on etching of the SiC without considerations of selectivity to Si and SiO_2, or etching profile. Furthermore, the basic etching mechanisms still needed to be explored.

In order to incorporate SiC films into Si VLSI technology, a selective and frequently anistropic etching process with respect to Si and SiO_2 is required [15]. To fully utilize plasma-assisted etching for SiC technology, one needs to explore and understand the effect of various plasma parameters including pressure, power, etching species, dilutants, etc. For example, for the SiC homo-device (MOSFET), a selectivity of SiO_2 to SiC higher than unity is required for gate area patterning and an anisotropic isolation etching process is needed for high density device applications. For the SiC/Si heterojunction device, fabrication considerations of SiC etching selectivity and anisotropy to define the active area are required. Therefore, various fluorinated gas mixtures, such as SF_6/O_2, $CBrF_3/O_2$ and CHF_3/O_2, have been investigated in this work in order to fulfill these requirements. Furthermore, the RIE etching mechanisms involved in using these gases, including both high fluorine-containing (SF_6) and low fluorine-containing gases ($CBrF_3$ and CHF_3) have been explored.

2. EXPERIMENTAL PROCEDURE

SiC thin films were deposited by RF sputtering onto silicon (100) substrates in a planar system. The film preparation and apparatus used in these experiments have been previously reported [9, 15]. The films were furnace annealed at 1100°C in a nitrogen ambient for 30 minutes. X-ray diffraction measurements exhibited a SiC (400) peak [16] indicating a polycrystalline film. The refractive index and thickness were determined using an ellipsometer at a wavelength of 632.8nm. n-type, 4-6 ohm-cm Si wafers were used to determine the Si etch rate. Oxidized silicon substrates (in steam at 1100°C) were used for SiO_2 etching. The etching experiments were carried out in a parallel plate reactor (Plasma Therm PK1241) equipped with a computer-controlled grating monochromator for measuring optical emission within the plasma. The corresponding wavelengths of each species were either obtained from Pearse and Gaydon [17] or determined experimentally. The DC self-bias of the RF electrode was also monitored. The fluorinated gases used in this investigation were CF_4 (99.9% purity), SF_6 (99.997%), $CBrF_3$ (>99%) and CHF_3 (>99%) and O_2 (99.99%).

The samples prepared for experiments were of size small enough such that the area ratio of sample-to-(power) electrode was less than 1%. Therefore, the samples did not disturb the plasma conditions during processing. To provide a suitable initial basis of comparison, the RF power, pressure and gas flow rate were generally kept constant at 200W (0.42W/cm^2), 20mTorr and 20sccm for all gases. Then, under a certain composition of gas mixture which exhibited the best SiC-to-Si etch rate ratio or the highest SiC etch rate, the power and pressure were changed independently to optimize the selectivity and etch rate.

To determine the etch rate in various ambients, Al was used as a thin film mask, since it is suitable for both low and high percentages of oxygen. The Al mask was subsequently removed by wet etching for step height determination using a profilometer. Samples with deeply etched patterns were used to observe the anisotropic etching phenomena by scanning electron microscopy. The composition versus depth profiles of both pre- and post-plasma etched SiC samples were obtained by Auger electron spectroscopy (AES) with a 5Kev Ar ion beam at the following energies: 92eV (Si), 272eV (C), 503eV (O), 647ev (F), 1396eV (Al). The system sensitivity factor for each element was used to normalize the peak intensity.

The concentrations of plasma species which are reactants during the etching process are not necessarily linearly proportional to their emission intensities. The optical emission measured during etching indicates the fraction of plasma species electronically excited into an emitting state and is, therefore, a function of both the density of species in the plasma and the electronic distribution. Noble gas (Ar or N_2) actinometry, wherein the excitation of the noble gas atom and the reactive particle have similar dependence on plasma parameters, has been previously used [18, 19] to obtain the relation between measured emission intensity and actual concentration of species in the plasma. In this work, Ar actinometry was used for this purpose and the relative concentrations of plasma species, such as F, O, H and Br were deduced from their emission intensities in different fluorinated gas mixtures [20, 21]. During experiments, a small amount of Ar gas, 0.6sccm (3% of total), was added to the constant total flow rate of 20sccm. A linearly increasing Ar (750nm) emission intensity with increasing Ar flow rate was observed, in agreement with previous results. The addition of the Ar gas to the feed does not alter the emission intensity of the other species present in the plasma under different etching gases and conditions. Therefore, all data presented in this work have been calibrated to their relative concentrations simply by dividing their emission intensity by the Ar emission intensity. Examples of normalized Ar

intensity in plasmas containing SF_6, $CBrF_3$ and CHF_3 plus oxygen were used to calculate relative species concentration in each gas.

The etching mechanism of each gas has been investigated by exposing SiC films of large area in the chamber. The surface coverage was from 10% to 40%. The backside of samples used in this experiment was covered by an aluminum film to avoid [F] consumption through reaction with the Si substrate. The changes in species density in the plasma caused by consumption of large amounts of reactants [22], such as [F] (703nm) and [O] (777nm), and the generation of by-products, such as [CO] (297nm) and [CF_2] (289nm), were easily detected from optical emission spectra. As usual, the [CO] and [CF_2] products could be formed by the process gases themselves in the plasma, such as in $CBrF_3$ and CHF_3. Therefore, a comparison spectrum was used to eliminate this effect from the experiments. The carbon products detected after baseline adjustment were considered to be contributed by the SiC only. The [CO_x] and [CF_x] intensity could be detected at many different wavelengths, such as 283nm, 297nm, 313nm for [CO], 290nm for [CO_2^+], 275nm, 262nm, 290nm for [CF_2], etc. The choice of wavelength monitored for each product was determined by the variation of intensity during etching by each processing gas.

3. RESULTS

The SiC etch rate was first determined as a function of oxygen percentage in SF_6 gas plasma. In Fig. 1(a) the SiC, Si and SiO_2 etch rates are shown as a function of oxygen percentage (from 0% to 90%) in SF_6 at a pressure of 20mTorr, total flow rate of 20sccm and power of 200W. The highest SiC etch rate measured is 53.3nm/min at 35%O_2, where the etch rates of Si and SiO_2 are 1.4μm/min and 60nm/min. The maximum Si etch rate, 2.1μm/min, occurs at 10%O_2. The SiC-Si etch rate ratio does not reach unity in SF_6/O_2

plasma, even at 90%O_2. The SiO_2 etch rate is similar to that of SiC. In Fig. 1(b) are shown the corresponding DC self-bias and the relative density of fluorine [F] (703nm) and oxygen [O] (777nm). A typical emission spectrum of SF_6/35%O_2 plasma at 200W, 20mTorr, 20sccm in RIE mode is shown in Fig. 2, where certain plasma products, such as [SO] (258nm), [SO_2] (315nm), [Ar] (750nm), [F] and [O], are identified at different wavelengths. The fluorine concentration reaches its maximum value at 30-40% O_2, then decreases as oxygen increases. The DC bias increases linearly from -285V at 0%O_2 to -400V at 90%O_2. Fixing the oxygen composition at 35%O_2, the pressure and power were varied to optimize the etching rate.

In Fig. 3(a) and (b), the etch rate versus pressure (from 20mTorr to 256mTorr) is shown along with the DC self-bias and the [F] and [O] densities for an RF power of 200W and a flow rate of 20sccm at 35%O_2. The SiC etch rate and the DC bias decrease rapidly when the pressure increased. The Si etch rate follows the trend of the fluorine density, reaching its maximum value of 5.34μm/min at 200mTorr. The highest reverse selectivity of SiC to Si is 1:267 at 200mTorr and the corresponding etch rate of SiC is 20nm/min. At 50mTorr, the SiC to SiO_2 etch ratio of 2.1:1 is obtained, where the etch rate of SiO_2 reaches its highest value, 76nm/min.

The pressure dependence experiment was repeated at a high percentage of oxygen in SF_6 plasma. Results are shown in Fig. 4(a) and (b) for SF_6/90%O_2, 200W, 20sccm plasma conditions. The SiC etch rate reaches its maximum etch rate, 50nm/min, at 68mTorr and then decreases as pressure increases. This behavior exhibits differences from the pressure dependence experiment in 30%O_2 plasma. A maximum etch rate of 46nm/min is measured for SiO_2 at the same pressure. The etch rate of Si increases monotonically with pressure, still basically following the variation of fluorine density even at such a high

composition of oxygen. The DC bias decreases linearly, while both oxygen and fluorine density increase as pressure increases.

The effect of varying the power from 50 to 300W on SiC etching in $SF_6/35\%O_2$ at 20sccm and 20mTorr is shown in Fig. 5. The etch rates of all samples increase linearly with increasing power up to 250W. When the power is higher than 250W, the etch rate of Si and SiO_2 and the fluorine density saturate. However, the SiC etch rate continues to increase with power and reaches its highest value of 100nm/min, in spite of the saturation in fluorine concentration. In Fig. 5(b), the variation of oxygen concentration with power is seen to be relatively small but monotonic, a 30% increase over the power range from 50W to 300W. An 83% increase in the fluorine concentration is obtained under the same conditions, but saturation is evident for power levels larger than 250W.

The etching results using $CBrF_3$ and O_2 mixtures in a similar etching experiment are shown in Fig. 6. The SiC etch rate increases linearly with oxygen percentage up to $75\%O_2$. The Si etch rate reaches its maximum value, 55nm/min, at $10\%O_2$ and then monotonically decreases with increasing $O_2\%$. A SiC to Si etch rate ratio of 2:1 is obtained at $75\%O_2$, where the etch rates of SiC and Si are 37.5nm/min and 18.8nm/min, respectively. The variation of SiO_2 etch rate with $O_2\%$ was minor, from 27nm/min at $0\%O_2$ to 28nm/min at $90\%O_2$. The DC bias and [F], [O], and [Br] (336nm) density are presented in Fig. 6(b).

The pressure dependence experiment of the etch rates in $CBrF_3/75\%O_2$ plasma, over the range 20mTorr to 215mTorr, is shown in Fig. 7. The SiC etch rate has a high and roughly constant value (40nm/min) from 20 to 50mTorr, then decreases with further increases in pressure. It is important to point out that even though the DC bias is monotonically decreasing with pressure, it only begins to affect the etch rate at values lower

than 300V, as shown in Fig. 7(b). In the high pressure region, high [Br] levels and low levels of [F] and [O] are detected. The SiC:Si etch rate ratio decreases from 2:1 at 20mTorr to 1:1 at 215mTorr.

The power dependence of the etch rates in $CBrF_3$/75%O_2 plasma is shown in Fig. 8. The etch rates of SiC and SiO_2 are seen to increase monotonically with increasing power, which is equivalent to DC bias. A sub-linear increase in Si etch rate with power was observed. The selectivity ratio is not improved by varying power over the 50 to 300W range. While both [Br] and [O] densities increase monotonically with power, the [F] concentration remains constant.

The etching data obtained for mixtures of CHF_3 and different percentages of O_2 are shown in Fig. 9(a) under the same plasma conditions as in previous experiments. The SiC etch rate increases with increasing O_2 composition, reaching a maximum value at 85%O_2 then decreasing to zero for pure O_2 plasma. The Si etch rate exhibits a similar trend, with the maximum occurring at 70%O_2. A maximum etch rate ratio of SiC to Si of 2:1 is obtained for CHF_3/90%O_2. For mixtures with less than 90%O_2, the SiO_2 etch rate is close to 40nm/min. In pure O_2 plasma, the etch rate is nearly zero for all samples. The corresponding DC bias, [F], [O] and [H] (486nm) densities are shown in Fig. 9(b). The highest fluorine density occurred between 75% and 85%O_2 and an average value of -410V was obtained for the DC bias over all values of oxygen percentage.

Results of pressure dependence experiments in CHF_3/90%O_2 plasma are shown in Fig. 10. Under conditions of 200W, 20sccm, the SiC-Si selectivity ratio decreases from 2:1 at 20mTorr to 1:1.1 at 315mTorr. The DC bias decreases monotonically with increasing pressure, as shown in Fig. 10(b) but only reaches -250V at 315mTorr. This is in contrast to the SF_6/90%O_2 case, where the DC bias was reduced to -250V at 150mTorr

and reached -70V at 340mTorr. A small increase in the etch rate with pressure is first evident. The SiC etch rate in $CHF_3/90\%O_2$ is seen to also vary less with pressure than in the case of $SF_6/90\%O_2$ or $CBrF_3/75\%O_2$ plasmas. This points out that a relationship evidently exists between the SiC etch rate and the value of the DC bias. As for the previous gas plasmas investigated, varying the RF power for the CHF_3/O_2 case results in the monotonic increase in etch rate for Si, SiC and SiO_2, as shown in Fig. 11(a). The selectivity ratio was close to 2:1 at all power levels. SiC and Si etch rates of 75nm/min and 33nm/min are obtained at 300W. The corresponding DC bias and plasma densities are displayed in Fig. 11(b).

The edge profiles obtained using these fluorinated gases were examined by SEM. In general, no undercut was observed, but rather a tapered profile of the SiC film edge was found. In the microphotograph of Fig. 12(a), it is shown that a vertical-to-lateral edge profile ratio of 10.3:1 has been obtained in an $SF_6/35\%O_2$ plasma at 200W, 20mTorr. The Si substrate underneath the SiC film was removed by isotropic etching and no backside etching of the SiC film was observed. The undercut of the Si substrate is not improved by increasing the power, since that induces a higher fluorine concentration. However, it is strongly reduced by using a high composition of oxygen in the plasma. In Fig. 12(b), an edge profile ratio of 11:1 is shown to result from using $SF_6/90\%O_2$ plasma. In this case only a small Si undercut, 50nm, is observed after etching 400nm into the Si substrate. A tapered profile ratio of 6.3:1 is obtained by using a $CBrF_3/75\%O_2$ plasma, as shown in Fig. 12(c), where the etching was stopped inside the SiC layer. In Fig. 12(d), an anisotropic ratio of 12.5:1 and no undercut of SiC or Si is obtained by using a $CHF_3/90\%O_2$ mixture. In this microphotograph, the SiC film is shown with the Al thin film mask in place. The edge ratio is reduced to 5.5:1 when the pressure was increased to 74mTorr at the same composition of plasma. The highest edge ratio of 17:1 is obtained for $CHF_3/90\%O_2$, 300W, 20mTorr.

The surfaces of SiC films, prepared by 3min etching at 200W, 20mTorr, 20sccm plasma conditions under different compositions of oxygen in each gas, have been analyzed by Auger electron spectroscopy (AES). An average sputtering rate of 1.2nm/min is measured for the 5keV Ar ion beam used in AES. After being calibrated and normalized to the system sensitivity, the resulting AES depth profiles for $SF_6/\%O_2$ are shown as an example in Fig. 13. A carbon rich surface was found at different concentration levels of oxygen in all gases. The atomic ratio of Si to C was close to unity before and after rapid furnace annealing of the SiC thin films. The surface carbon concentration was reduced by increasing oxygen concentration in the plasma. When a pure oxygen plasma was used, the surface was oxidized. Therefore, removing the carbon layer from the etching surface is believed to be the rate-limiting step for etching SiC. A high [F] intensity was observed only for SF_6/O_2 plasma etching. No measurable [Al] intensity was observed in all cases. Therefore, the use of an Al electrode and an Al mask for experiments were not considered to have a contamination effect under these plasma conditions, unlike the observation reported by Palmour et al. [11] on Al micromask effects causing a rough etching surface.

Mass loading effects on the plasma etching of SiC in SF_6/O_2 mixtures was investigated. Four 3" diameter SiC thin film samples (40% coverage) were used during etching by $SF_6/35\%O_2$ at 200W, 20sccm, 20mTorr. The DC bias, [F] (703nm), [O] (777nm), [CF_2] (289nm) and [CO] (297nm) intensity were monitored. In Fig. 14(a), the intensity of comparison spectrum is shown, displaying the difference between the "no sample" plasma (positive part) case and the SiC sample loaded plasma (negative part) case. The main reactants and products are marked. The data for [CO], [F] and [O] density versus etching time is displayed in Fig. 14(b), starting with unloaded plasma (time < 0), followed by the time period of etching the SiC film (from $0 \leq$ time < 3.5min) and finishing with etching of the Si substrate. The [CO] density was measured from the comparison

spectra. Both [F] and [O] density decreased during the etching cycle. The [CO] density indicates a clear relationship to the etching cycle. No [CF_2] peak was found. Similar results were observed for experiments using SF_6/90%O_2, $CBrF_3$/70%O_2, CHF_3/90%O_2 plasmas.

4. DISCUSSION

In this section we discuss certain aspects of the SiC plasma etching experiments relevant to understanding the mechanisms at work. Reactive ion etching in SF_6/O_2 plasmas is distinguished by the largest generation of fluorine concentration observed compared to the other investigated gas mixtures. This results in the highest Si etch rate levels (by a factor 2-3) and in an etch rate dependence on oxygen percentage in the plasma which is related to, but does not exactly follow, the fluorine density. The main etching mechanism of Si in the SF_6 plasma involves the chemical reaction between silicon and fluorine atoms with the formation of volatile compounds [23]. The chemisorption [24] of oxygen on the Si surface reduces the availability of etching sites and thus decreases the Si etch rate. Therefore, a shift results in the maximum Si etch rate from the O_2 percentage of maximum [F] density (35%) to a lower O_2 percentage (10%). For SiC etching, oxygen chemisorption is not considered to have a strong effect, since carbon can react directly with oxygen. The SiC-to-Si etch rate ratio in SF_6/O_2 plasmas is much smaller than unity for the entire range of parameters investigated. Increasing the oxygen concentration and DC bias by using a higher percentage of oxygen enhances the chemical reaction of carbon and oxygen, but depresses the effect of fluorine due to the reduced fluorine concentration. A fairly high (10 to 1) etching anisotropy was observed for SF_6/O_2 etched SiC films, as shown in Fig. 12. The presence of the C-rich surface determined from AES combined with the lack of backside etching of the SiC film suggests that a protective carbon blocking layer is formed. The upper surface of the SiC films is exposed to energetic ion

bombardment which can remove the blocking layer by a combination of physical sputtering and ion-assisted chemical reaction between carbon and oxygen.

The effectiveness of ion bombardment is a function of the ion energy in the plasma, which in turn is related to the DC potential generated in the plasma. In the SF_6/O_2 plasma, when the pressure was increased from 20 to 256mTorr (Fig. 3), the DC bias decreased rapidly from 350 to 25V. The SiC etch rate strongly followed the change of DC bias even though both F and O concentrations increased. A critical DC bias was observed in the $SF_6/90\%O_2$ pressure experiment (Fig. 4). When the DC bias was higher than 300V, the etch rate of SiC appears to be determined by the availability of gas phase reactants, namely oxygen and fluorine. The SiC etch rate reached its maximum value of 50nm/min and stayed at a level above 40nm/min up to the point where the DC bias dropped below 300V. Therefore, the DC bias is considered to be the key factor controlling the reaction between carbon and oxygen, while the reaction between fluorine and Si can take place at low ion energy. Increasing the power level (Fig. 5) indicates that higher reactant concentration and higher ion energy were induced by the plasma resulting in a higher etching rate for all samples. Almost no lateral etching was observed even when the percentage of oxygen was increased to $90\%O_2$, where the anisotropic ratio was 11:1. The undercut of the Si substrate was improved by reducing the chemical reaction through low fluorine concentration and by increasing the DC bias.

In $CBrF_3/O_2$ plasmas, as shown in Fig. 6, the density of [F] and [O] is much smaller than in the corresponding SF_6/O_2 plasma. Consequently, the Si etch rate is dramatically reduced, by a factor of approximately 10 to 30. The SiC etch rate was also reduced, but only by a factor of 1.5-2. Therefore, for oxygen percentage in the plasma greater than 60%, the relative abundance of oxygen compared to the near absence of fluorine results in a SiC-to-Si etch rate ratio greater than unity. At $CBrF_3/75\%O_2$, a

selectivity of 2:1 is observed. Under these conditions, a SiC line edge anisotropy of 6.3:1 was measured (see Fig. 12). The DC bias decreased from 420V to 160V, when the pressure was increased from 20mTorr to 215mTorr, as shown in Fig. 7. When the pressure was lower than 100mTorr, or the DC bias higher than 300V, the SiC etch rate ranged within a 5% band from 38nm/min (at 20mTorr). However, above 100mTorr, the SiC etch rate followed the same trend as the DC bias, which is similar to the $SF_6/90\%O_2$ pressure experiment. The linearly increasing etch rate and species density was caused by the increasing plasma power in the power experiment shown in Fig. 8. The effects of bromine atoms in the etching process and on the line edge ratio are not quite clear yet and need further investigation.

In CHF_3/O_2 plasma, the presence of hydrogen mainly depresses the [F] intensity, with the oxygen intensity reaching levels similar to the SF_6/O_2 plasma. The peaks in [F] and [O] density occur for 70% and 90% O_2 mixtures, respectively. The Si etch rate variation with O_2% tracked the [F] density well and decreased very fast with lowered fluorine density and chemisorption of oxygen on the surface in the high oxygen density region. On the contrary, the SiC etching condition reaches the optimum conditions in this situation, since it provides high DC bias (high ion energy), sufficient fluorine density (to remove Si atoms) and high concentration of oxygen (to remove C atoms). The maximum SiC etch rate, 47nm/min, occurred for an $80\%O_2$ mixture, while the maximum SiC:Si selectivity of 2 was measured for the $90\%O_2$ mixture. The high (415V) and almost constant (with O_2%) DC bias found in this case produced the highest anisotropic ratio (12.5:1) achieved.

Changes in pressure in the CHF_3/O_2 plasma (see Fig. 10) resulted in a SiC etch rate variation similar to that observed for SF_6/O_2 and $CBrF_3/O_2$ gases. For a DC bias higher than 300V, the SiC etch rate appears limited by the reaction rate between carbon and

oxygen. In the low DC bias case the SiC etch rate was shown to be strongly dependent on DC bias rather than on the (high) density of reactants ([F] & [O]). Therefore, the selective etch ratio of SiC to Si decreased from 2:1 at 20mTorr to 1:1.1 at 315mTorr. The linear relation between etch rate and DC bias was observed in the power experiment for $CHF_3/90\%O_2$, shown in Fig. 11. The higher ion energy enhanced almost all reactions, and thus no better selectivity ratio was obtained. A very high anisotropic ratio, 17:1, was, however, obtained by using the higher power level of 300W.

For selective etching of SiC to SiO_2, the maximum ratio of 1.3:1 was obtained in $CHF_3/80\%O_2$. The optimum reverse selectivity of 1:3.6 was measured in pure CHF_3 plasma. In SF_6/O_2 and $CBrF_3$ plasmas, the SiO_2 etch rate is quite similar to that of SiC and no selectivity was observed. A summary of results of selective and anisotropic ratios of SiC/Si and SiC/SiO_2 is shown in Table 1.

Additional SiC etching experiments were performed to investigate loading effects. For these experiments oxidized Si substrates were used since the SiO_2 presents a sharper color change from SiC (green) to SiO_2 (dark red). The SiC film thickness at the wafer edge was 10% thinner than in the center region, due to a sputtering effect, resulting in a "ring" effect where the SiO_2 underlayer is reached. Fig. 15 displays the etching patterns obtained by using four gas mixtures under the same plasma conditions (200W, 20mTorr and 20sccm): $SF_6/35\%O_2$, $SF_6/90\%O_2$, $CBrF_3/75\%O_2$ and $CHF_3/90\%O_2$. For the low concentration oxygen case, such as $SF_6/35\%O_2$, when a 3" SiC-covered wafer was loaded the etch rate at the wafer edge close to the gas inlet was faster than at the edge close to the exhausting hole (center). We can assume that the oxygen concentration was depleted along the direction of flow. Thus, in this case the etching of SiC is dominated by the mass-transfer rate. In the high concentration oxygen case, such as the $SF_6/90\%O_2$ or $CHF_3/90\%O_2$, the reaction-rate dominates the etching. Because of the variation of film

thickness, the etching pattern observed was round and symmetric. The effect of the carbon-rich surface in SiC etching is presumably the rate-limiting step. The oxygen has a strong effect in removing this carbon layer and improves the SiC etch rate, while the fluorine was shown not to be a major reactant for removing carbon under these etching conditions.

Based on the experimental results discussed above, we conclude that the reactive ion etching of SiC consists of two basic mechanisms: chemical reaction and physical removal process. For SiC and Si etching in fluorinated gases the most likely chemical reactions are given below:

$$Si + 4F \rightarrow SiF_4 \quad \ldots\ldots (1)$$

$$C + xO \rightarrow (CO, CO_2) \quad \ldots\ldots (2)$$

$$SiC + xF + yO \rightarrow SiF_4 + (CO, CO_2) \quad \ldots\ldots (3)$$

In reaction (1), Si is removed mainly by reacting with fluorine to form SiF_4 volatile molecules [23] at room temperature. The energy required for this reaction is believed to be much lower than the energy needed for the oxygen-carbon reaction of eq. 2. As observed in the $SF_6/35\%O_2$ experiments as a function of pressure, shown in Fig. 3, the Si etch rate followed the variation of fluorine density, even though the DC bias was as low as 25V. Carbon can react with either fluorine or oxygen atoms but only carbon mono- or dioxide products were directly observed in our etching experiments. No carbon fluoride product was identified from emission spectra even in cases of abundant fluorine concentration , such as the $SF_6/35\%O_2$ loading experiments. Hence, only oxygen is considered in the reaction of eq. 2, whereas the reaction between carbon and fluorine is suggested to occur at a very low rate. Therefore, in the etching of SiC, the two-step etching process shown in eq. 3 is considered to be an appropriate model, wherein silicon and carbon atoms are removed separately.

Also based on experimental results presented above, we postulate two regimes for the bias dependence of the SiC etch rate. As shown in Fig. 16, in regime I, the etching of the SiC films is rate controlled by the DC bias. In region II, above a critical value of the bias, the etch rate becomes reaction-limited. Since the Si is readily etched by fluorine even at low bias levels, we conclude that it is the reaction between carbon in the SiC and oxygen in the plasma that controls the SiC etch rate and needs to be enhanced by the DC bias. Under most conditions, the Si etch rate is higher than that of SiC. This is due to comparatively higher removal rate of Si atoms than C atoms. As a result, a carbon-rich surface is formed on the SiC film during etching, becoming a potentially rate-limiting step under certain conditions. The C-rich surface has been verified by Auger electron spectroscopy (AES) and could be reduced by increasing oxygen concentration and DC bias.

A carbon sidewall blocking model is proposed (see Fig. 17) to explain the physical etching mechanism in reactive ion etching of SiC. In general, surface damage and inhibitor mechanisms [25, 26] have been used to understand the anisotropic etching caused by ions in plasma etching. The result of ion bombardment caused by the plasma-induced DC bias on the electrode carrying the samples will cause a more directional etching and will generate more etching sites. However, ion bombardment is less effective at removing material from the sidewall (parallel to the ion direction). Therefore, a carbon-rich surface remains on the SiC sidewall reducing the lateral etching, thus, resulting in a more highly anisotropic etching. The carbon layer was assumed to be the only type of inhibitor present under such high oxygen concentration conditions. In Fig. 17(b), the carbon blocking layer model is used to explain the etching phenomena in the strong Si substrate undercut situation observed in SF_6/35%O_2 plasma (Fig. 12). In this case the SiC layer was protected by this

carbon layer and no etching from backside, especially by nondirectional neutral fluorine atoms, was observed, suggesting that fluorine atoms will not react with the carbon layer.

5. SUMMARY AND CONCLUSIONS

The reactive ion etching of SiC thin films in various fluorinated/oxygen mixtures has been investigated. The dominant factors of the SiC etch rate were indicated and discussed. The SiC etch rate appears to be controlled by a combination of physical (DC bias) and chemical (fluorine and oxygen density) mechanisms. A chemical reaction model and carbon-blocking models have been established, agreeing qualitatively with experimental results. A critical DC bias level appears to separate the regimes of chemical and physical rate-limiting step domination of the etch rate. No evidence was obtained in these experiments for fluorine reacting directly with carbon. An etch rate ratio of SiC to Si of 2:1 was obtained by using $CBrF_3$/75%O_2 and CHF_3/90%O_2 plasma. Good anisotropic profiles were obtained by RIE in CHF_3/90%O_2 and SF_6/35%O_2 plasma.

In general, in order to obtain selective SiC to Si etching, one needs to increase the oxygen concentration to enhance the SiC etch rate and to depress the fluorine concentration to reduce the Si etch rate. These conditions can be satisfied by choosing low-fluorinated gases (such as CHF_3, $CBrF_3$) and operating at a high oxygen percentage. A certain ion energy (DC bias) is considered to be particularly important for SiC etching.

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LIST OF FIGURES AND TABLES

Fig. 13 The AES depth profile of SiC etched in SF_6/% O_2: (a) as deposited; (b) 15%; (c) 35%; (d) 75%.

Fig. 14 Loading experiment by etching four 3" SiC wafers in SF_6/35%O_2: (a) comparison spectrum; (b) relative [F], [O], [CO] density.

Fig. 15 SiC etching phenomena by different gases and composition of oxygen at 200W, 20sccm, 20mTorr in RIE mode.

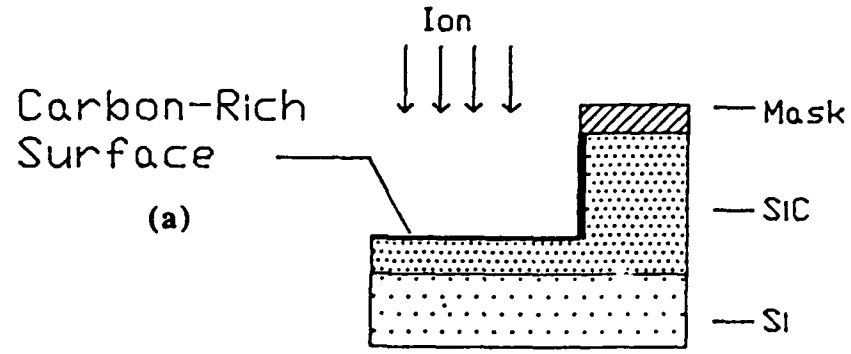
Fig. 16 Schematic of SiC etch rate dependence on plasma DC bias.

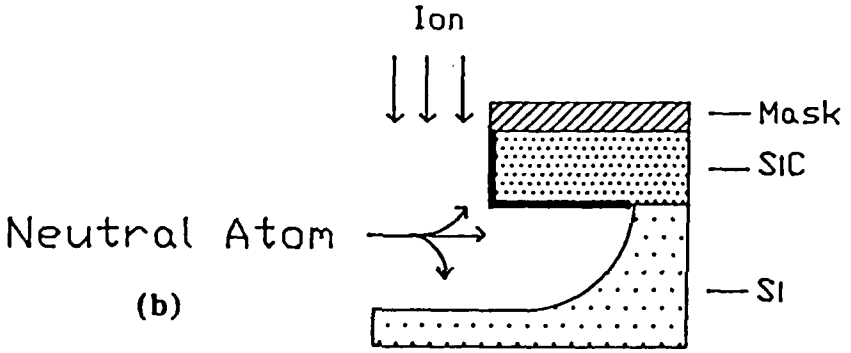
Fig. 17 Carbon-blocking model: (a) SiC anisotropic profile; (b) strong undercut of Si substrate.

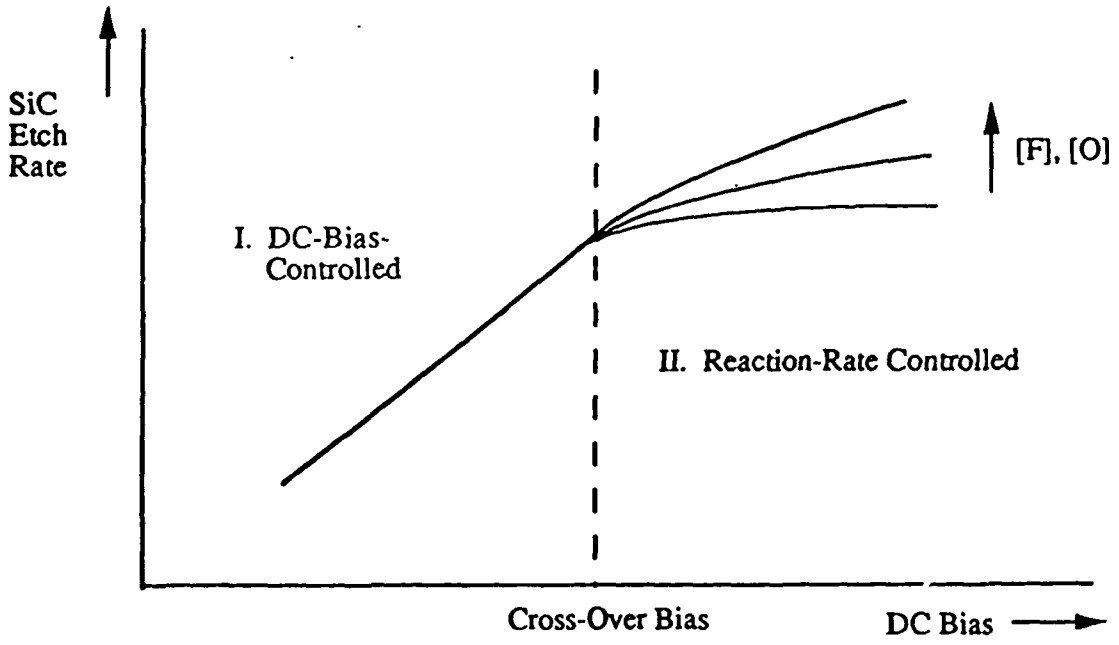
Table 1. Summary of reactive ion etching of SiC by different fluorinated gases and oxygen plasma.

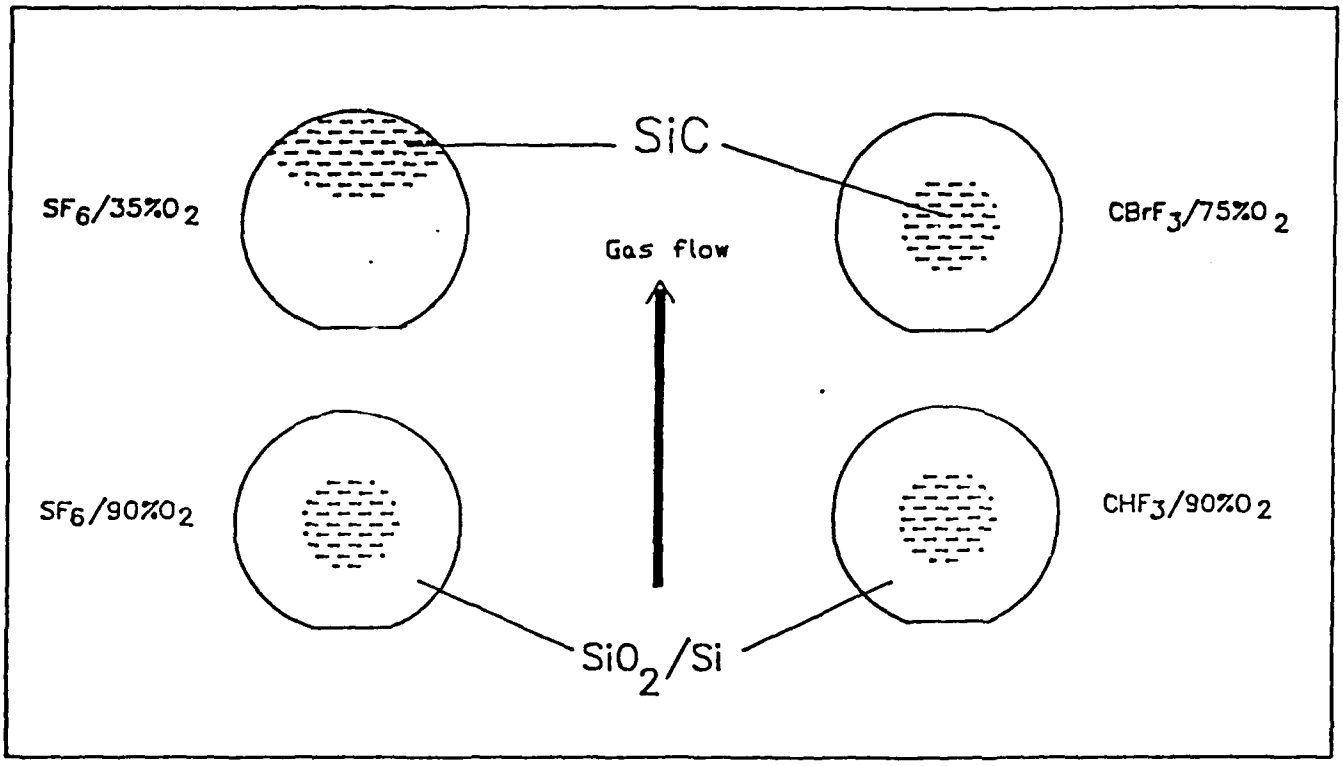
Table 1 SiC Reactive Ion Etching (RIE)

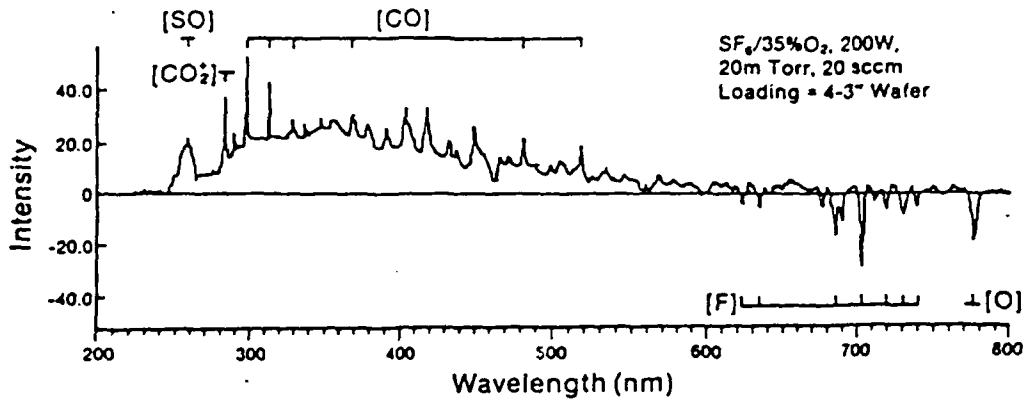
Gases	Power (W)	Pressure (mTorr)	Edge Profile Ratio*	Selectivity SiC : Si	Etch Rate SiC (nm/min)
CHF_3+90%O_2	200	20	12.5 : 1	2.0 : 1	41.7
	200	74	5.5 : 1	1.9 : 1	53.3
	300	20	17.0 : 1	2.0 : 1	75
$CBrF_3$+75%O_2	200	20	6.3 : 1	2.0 : 1	37.5
	200	72	7.6 : 1	1.8 : 1	39
	300	20	4.0 : 1	1.3 : 1	50
SF_6+35%O_2	200	20	10.3 : 1	1 : 26	53.3
	200	200	-------	1 : 267	20
SF_6+90%O_2	200	20	11.0 : 1	1 : 1.8	40
				Selectivity SiC : SiO_2	
CHF_3	200	20	-------	1 : 3.6	
CHF_3+80%O_2	200	20	-------	1.3 : 1	

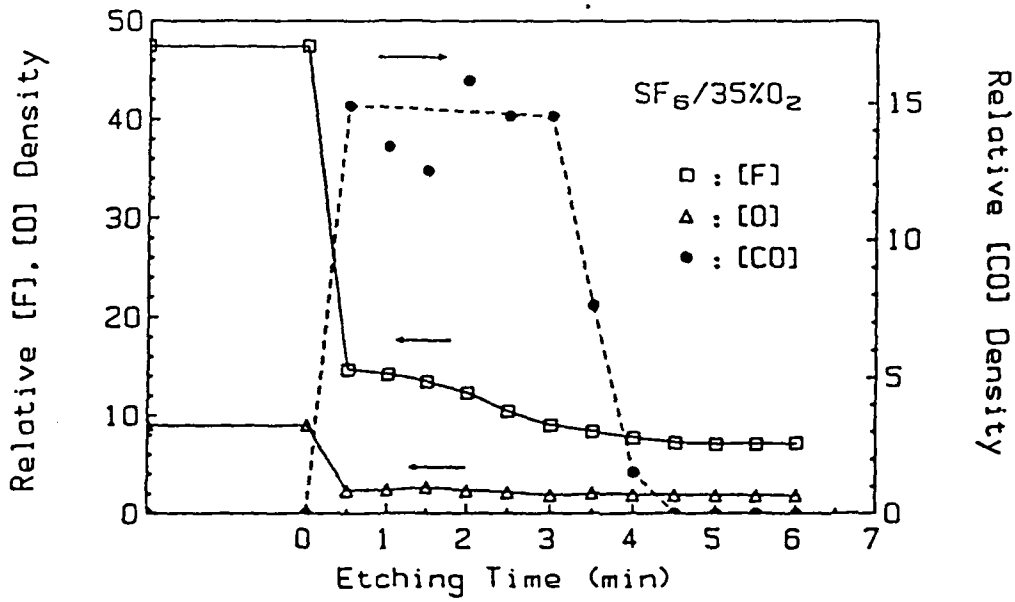

Ion
Carbon-Rich
Surface
(a)
Mask
SIC
SI


Ion
Mask
SIC
Neutral Atom
(b)
SI


SiC
Etch
Rate
I. DC-Bias-
Controlled
II. Reaction-Rate Controlled
[F], [O]
Cross-Over Bias
DC Bias


SiC
$SF_6/35\%O_2$
$CBrF_3/75\%O_2$
Gas flow
$SF_6/90\%O_2$
$CHF_3/90\%O_2$
SiO_2/Si


[SO]
[CO]
$[CO_2^+]$
$SF_6/35\%O_2$, 200W,
20m Torr, 20 sccm
Loading = 4-3" Wafer
Intensity
40.0
20.0
0
-20.0
-40.0
[F]
[O]
200
300
400
500
600
700
800
Wavelength (nm)


Relative [F], [O] Density
Relative [CO] Density
$SF_6/35\%O_2$
□ : [F]
△ : [O]
● : [CO]
50
40
30
20
10
0
15
10
5
0
0
1
2
3
4
5
6
7
Etching Time (min)

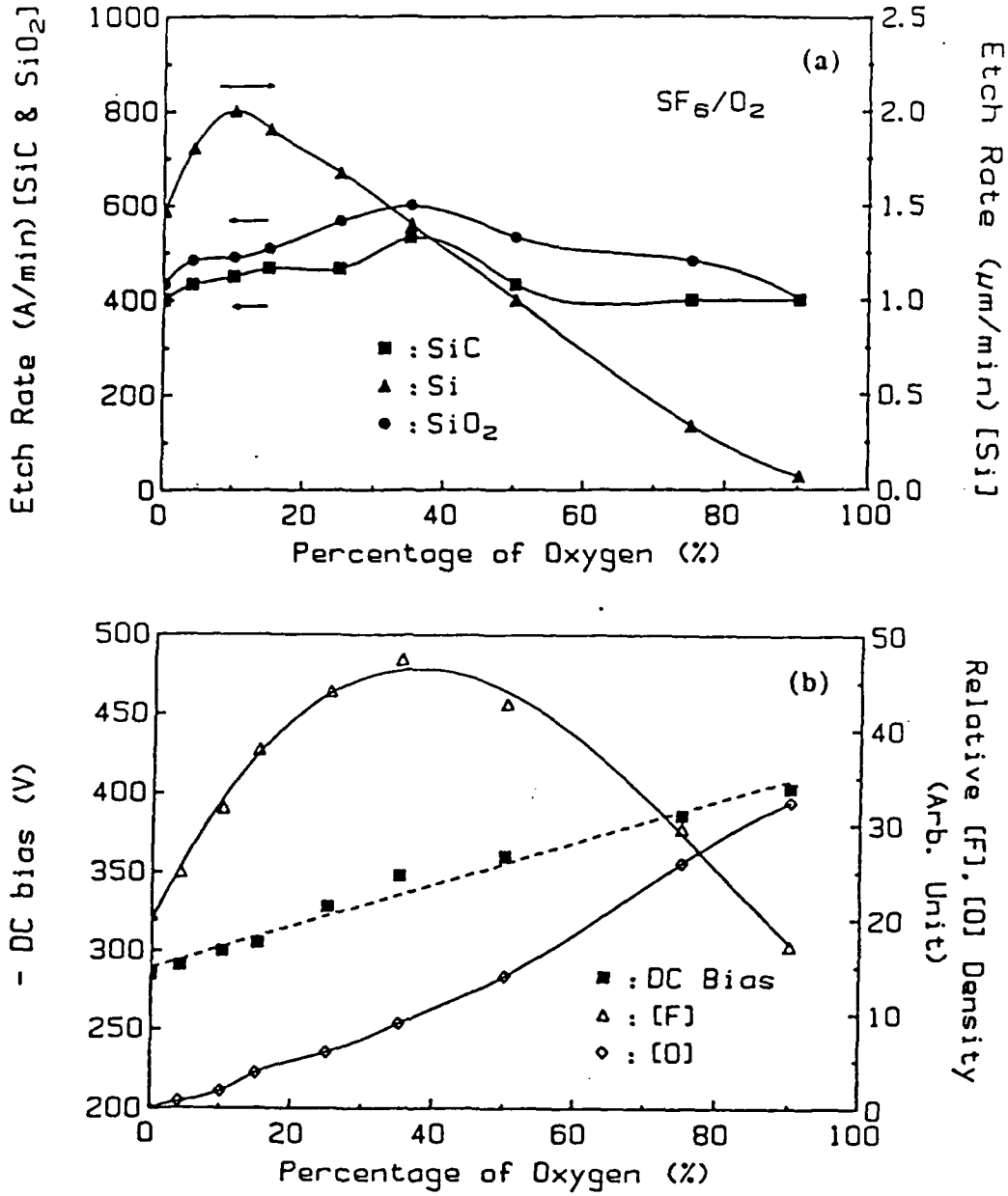
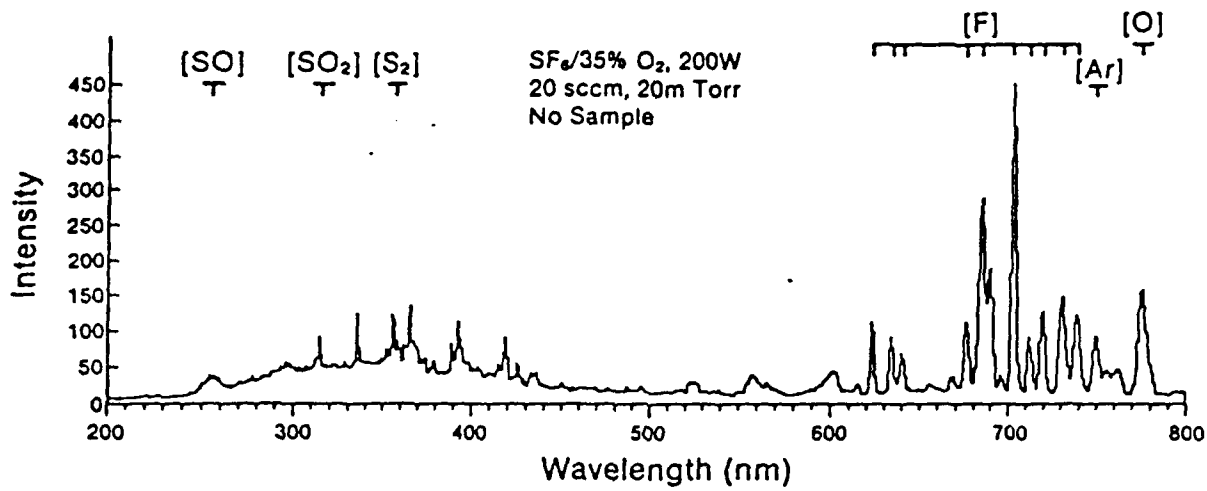
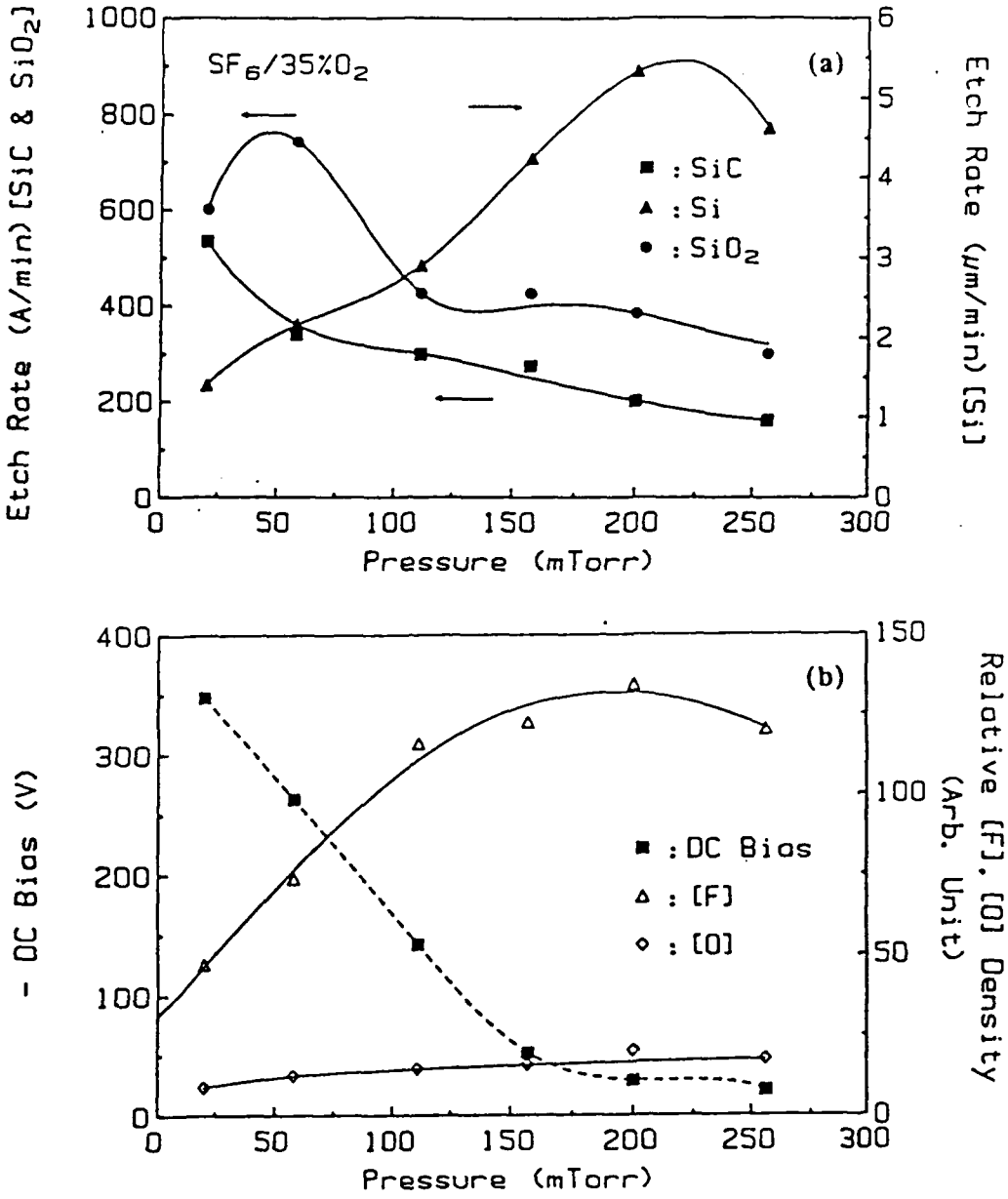
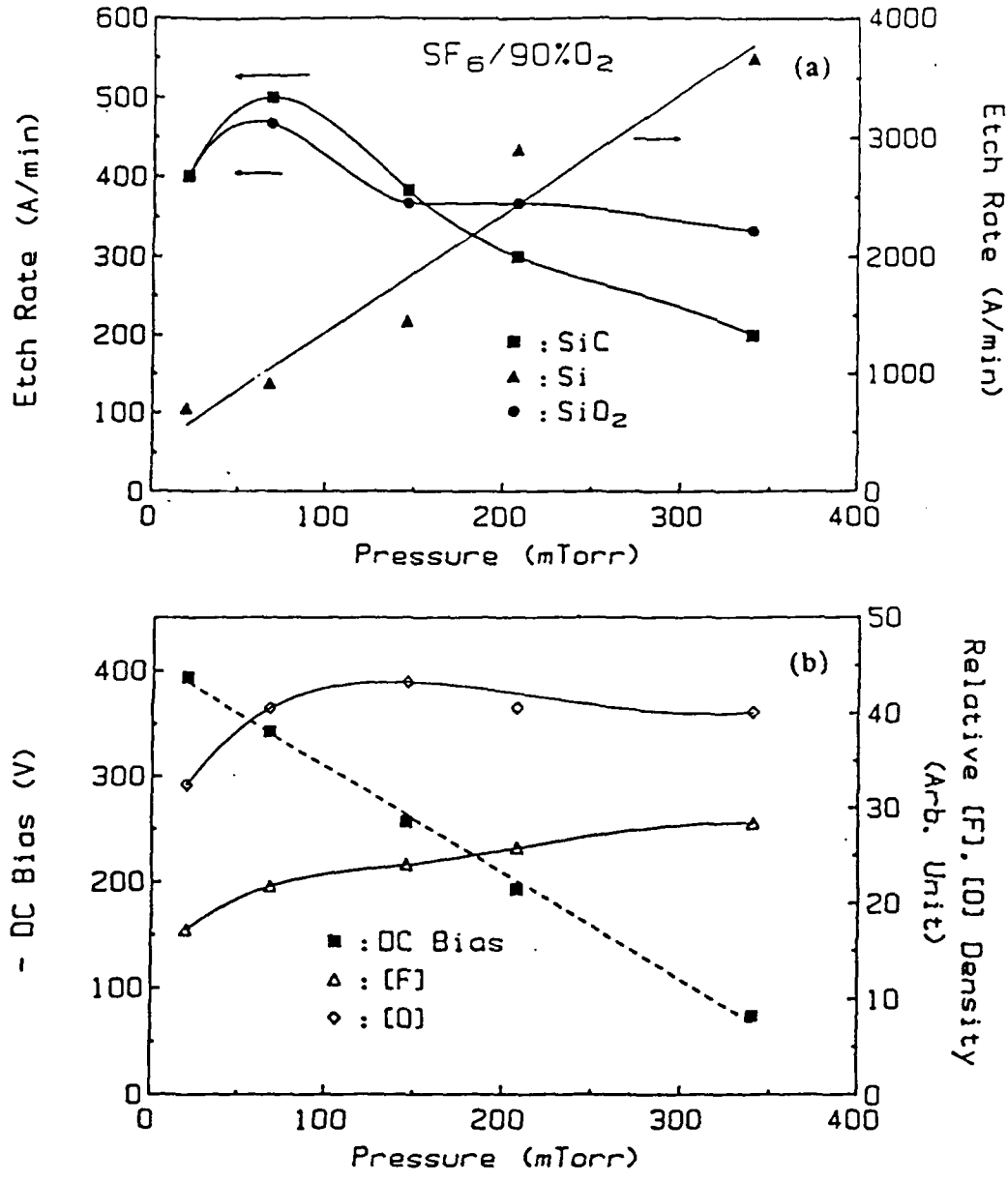
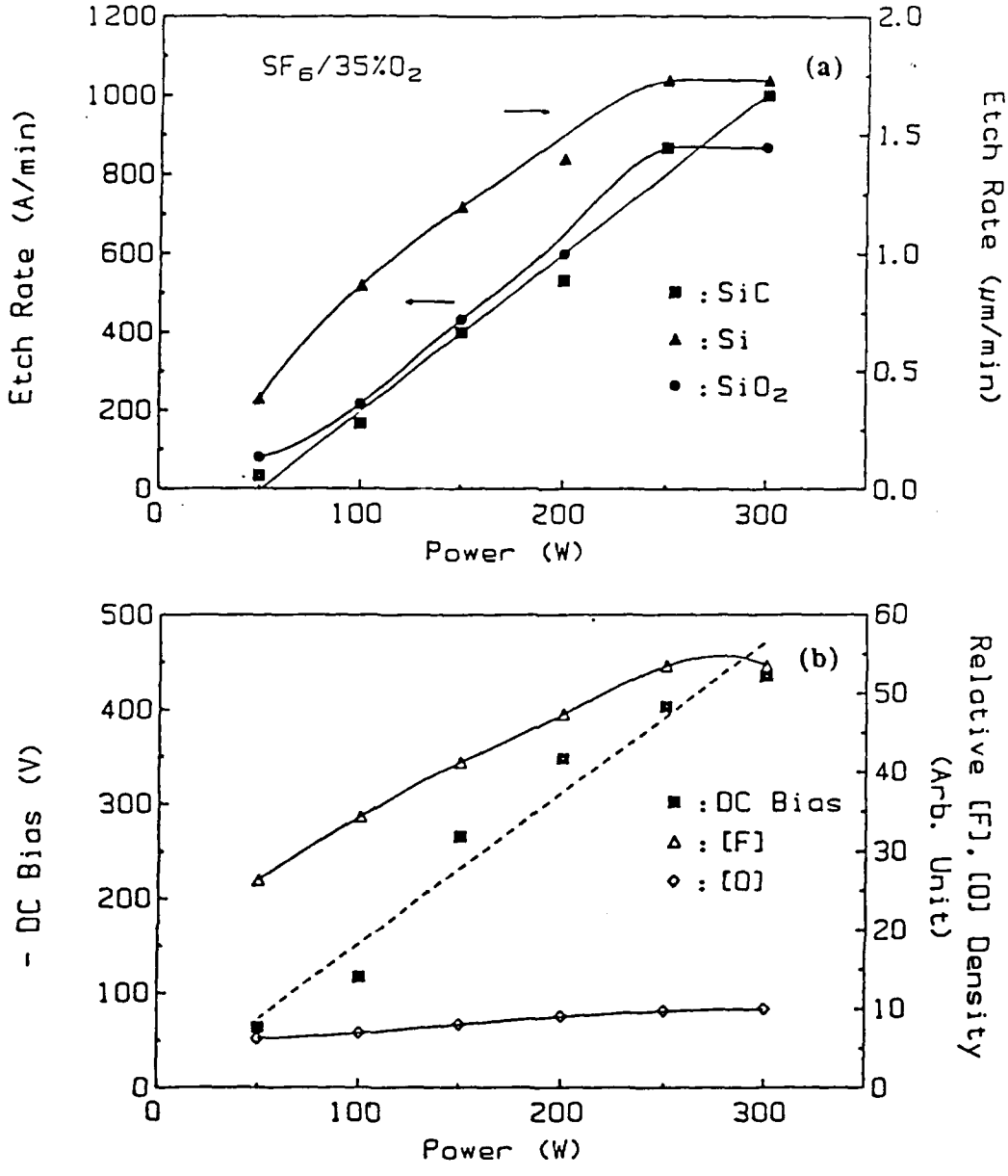


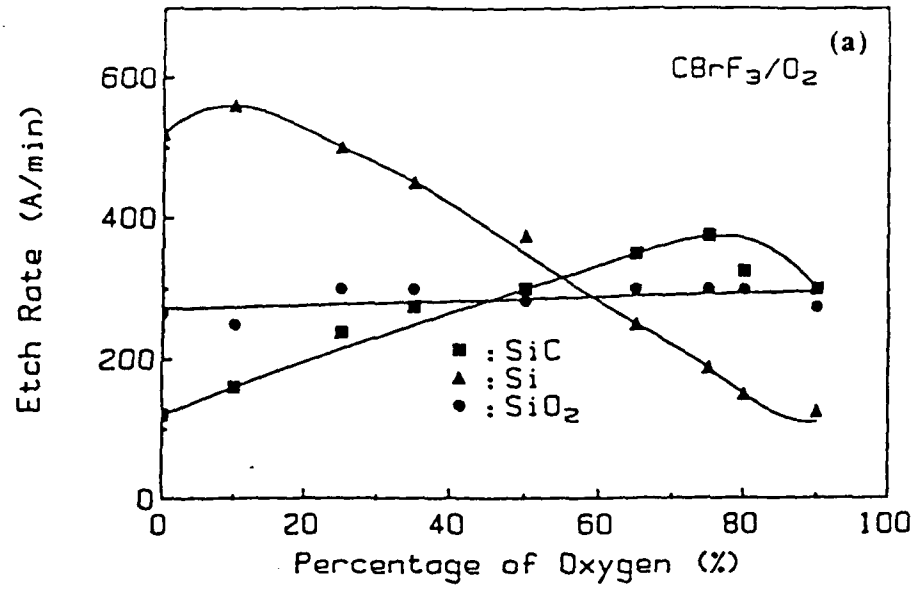
Fig. 1 Prior art

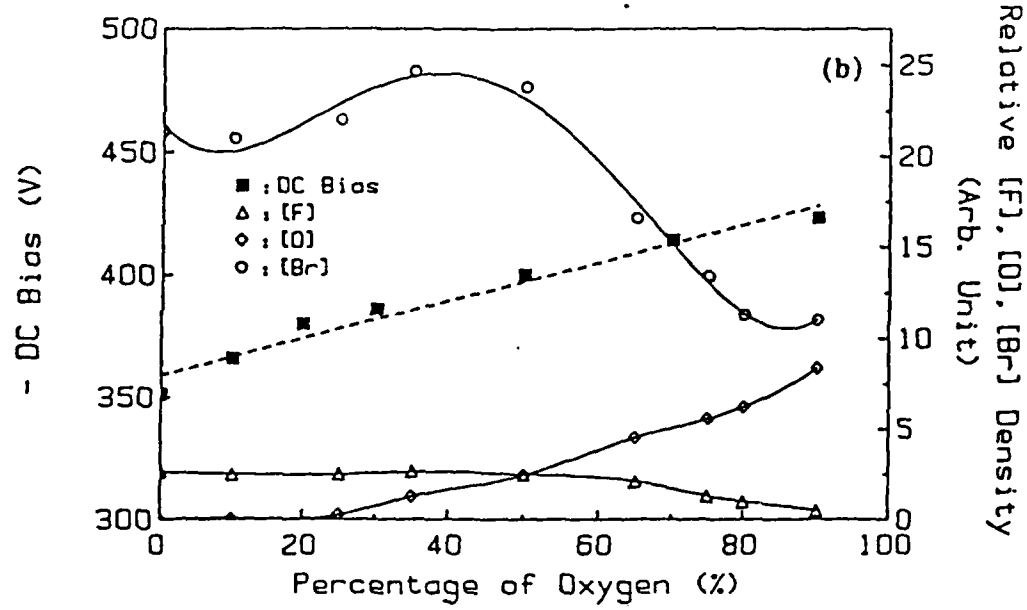

[SO]
[SO2]
[S2]
SF6/35% O2, 200W
20 sccm, 20m Torr
No Sample
[F]
[O]
[Ar]
Intensity
450
400
350
300
250
200
150
100
50
0
200
300
400
500
600
700
800
Wavelength (nm)

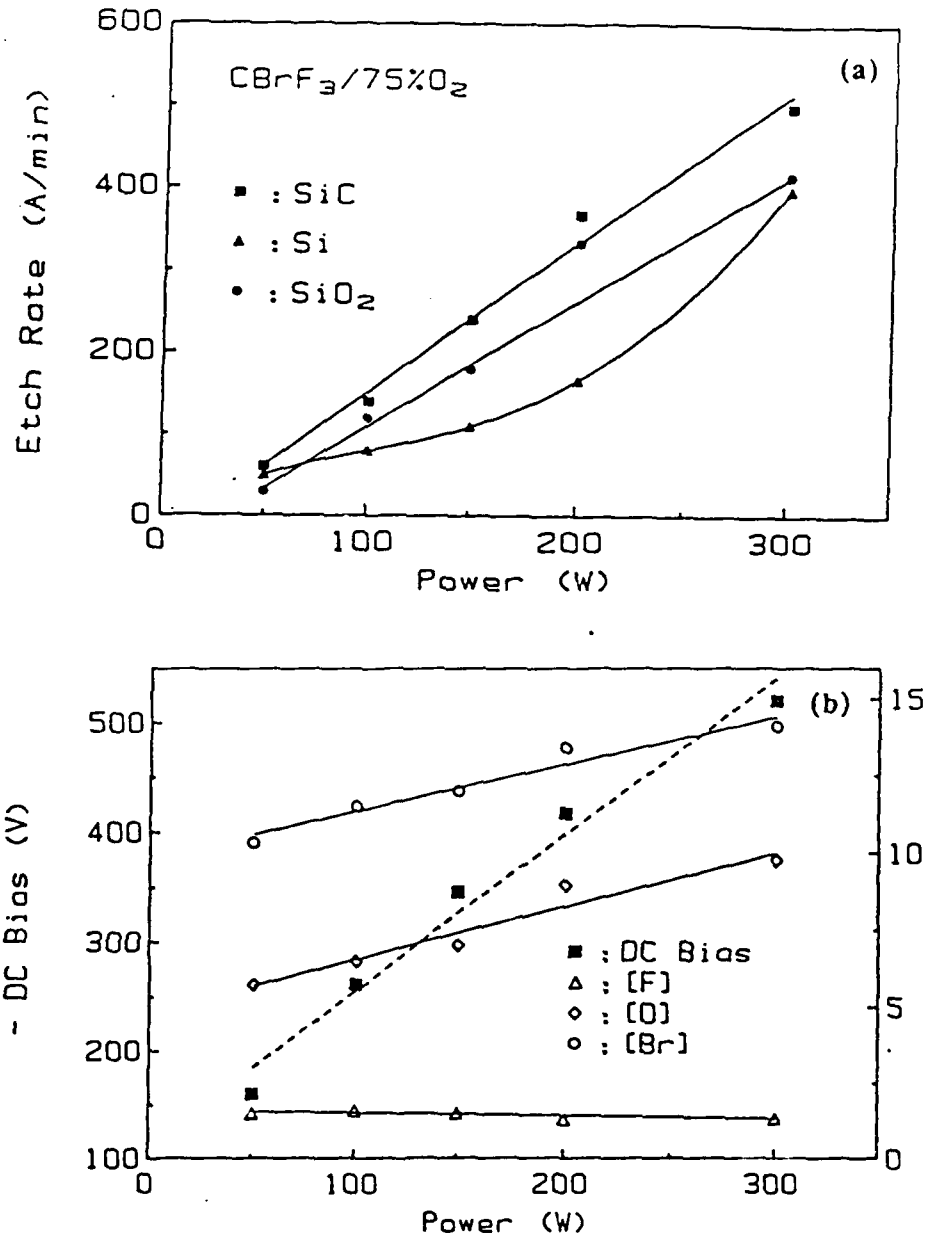

SF6/35%O2
(a)
■ : SiC
▲ : Si
● : SiO2
Etch Rate (A/min) [SiC & SiO2]
Etch Rate (μm/min) [Si]
Pressure (mTorr)
(b)
■ : DC Bias
△ : [F]
◇ : [O]
- DC Bias (V)
Relative [F], [O] Density (Arb. Unit)
Pressure (mTorr)

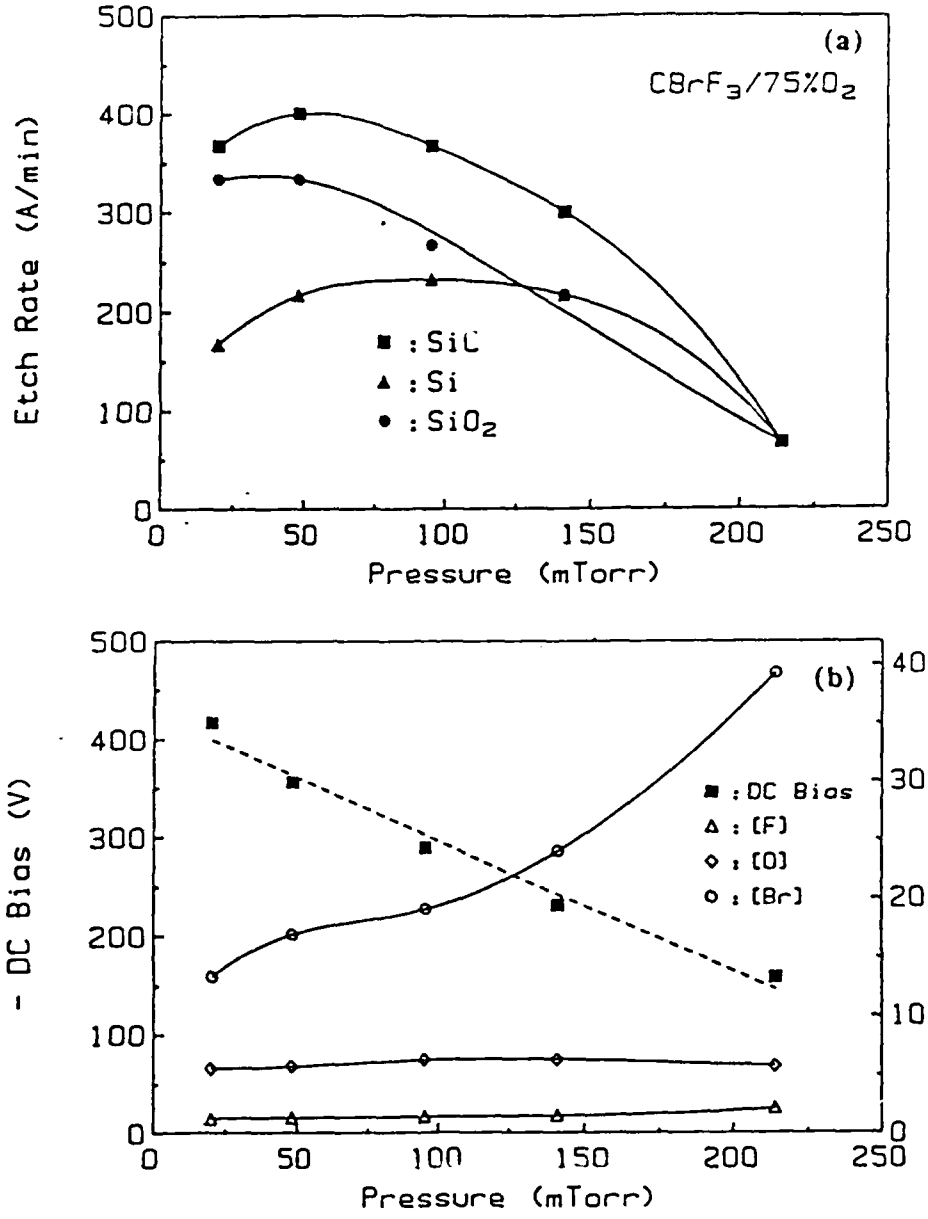

SF6/90%O2
(a)
Etch Rate (A/min)
Etch Rate (A/min)
: SiC
: Si
: SiO2
Pressure (mTorr)
(b)
- DC Bias (V)
Relative [F], [O] Density
(Arb. Unit)
: DC Bias
: [F]
: [O]
Pressure (mTorr)

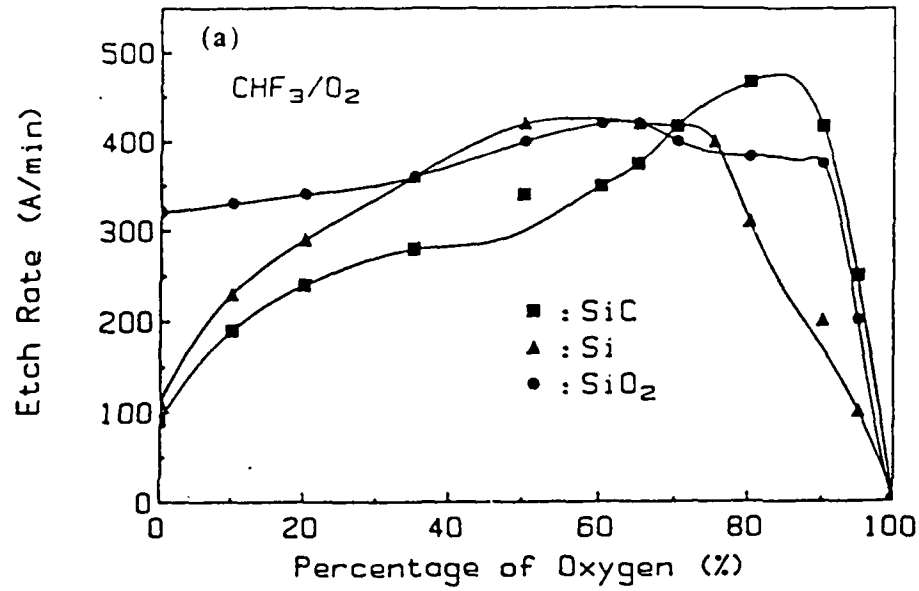

SF6/35%O2
(a)
Etch Rate (A/min)
Etch Rate (μm/min)
: SiC
: Si
: SiO2
Power (W)
(b)
- DC Bias (V)
Relative [F], [O] Density (Arb. Unit)
: DC Bias
: [F]
: [O]
Power (W)

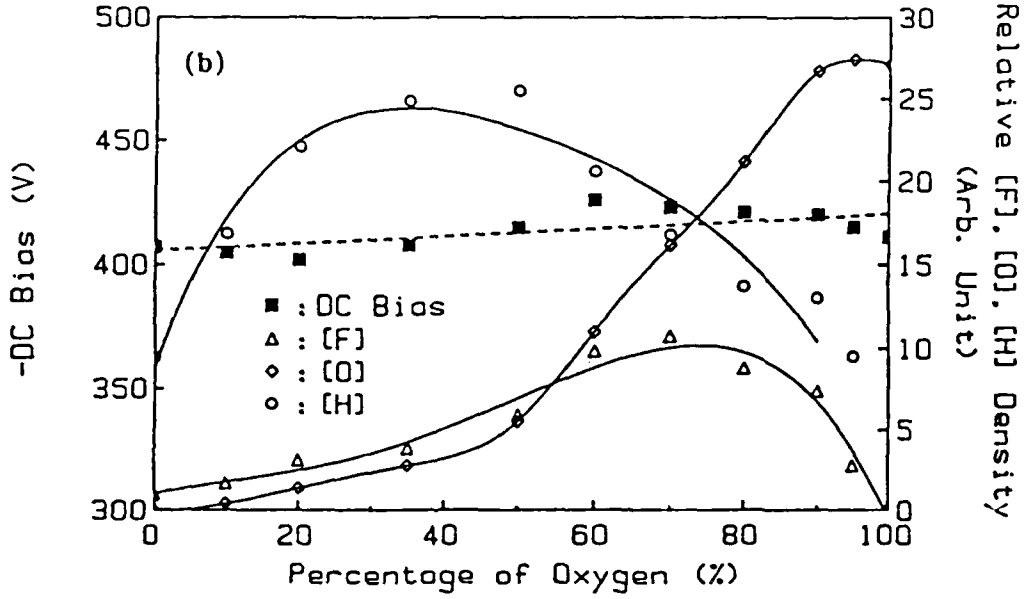

(a)
C_8F_3/O_2
Etch Rate (A/min)
600
400
200
0
0
20
40
60
80
100
Percentage of Oxygen (%)
■ : SiC
▲ : Si
● : SiO_2

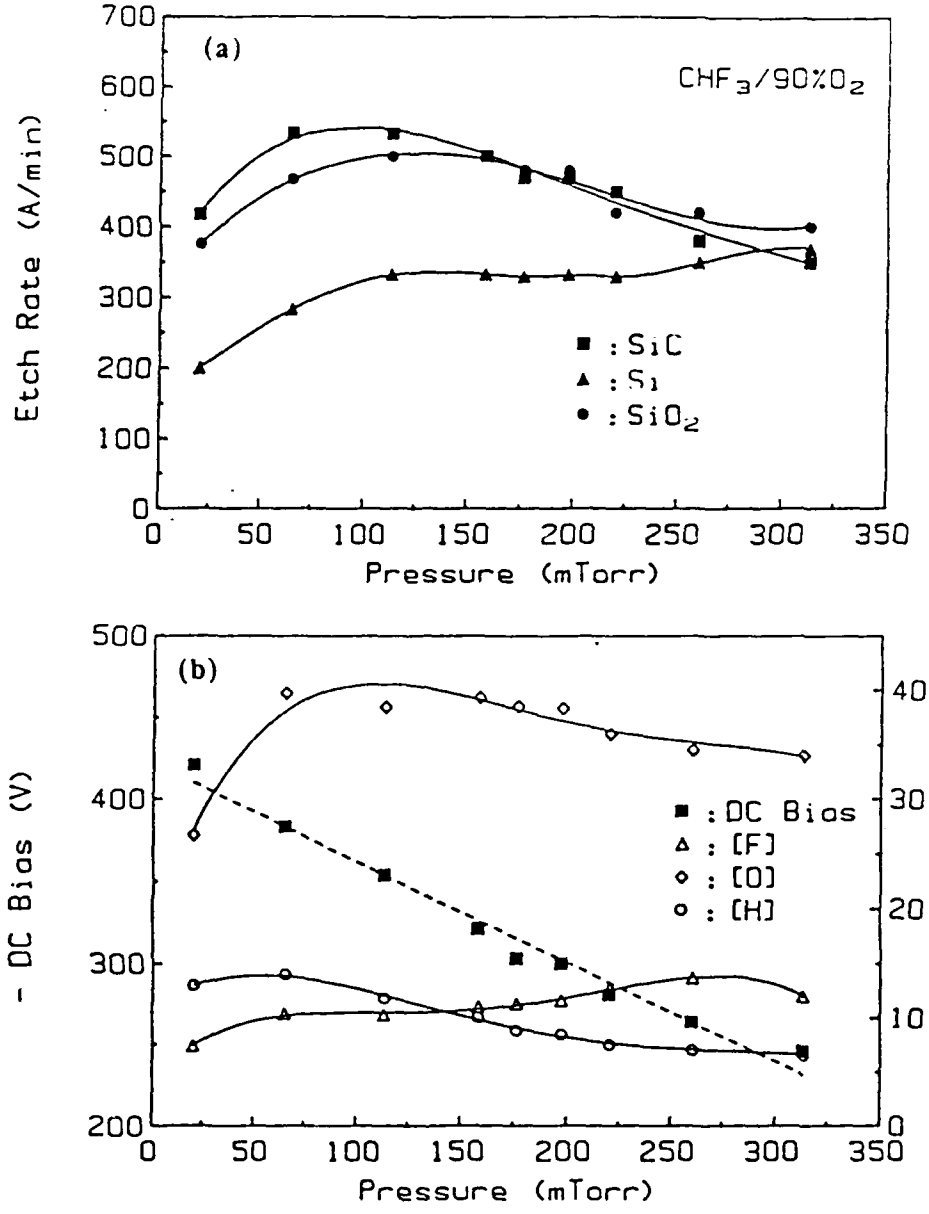

(b)
- DC Bias (V)
500
450
400
350
300
0
20
40
60
80
100
Percentage of Oxygen (%)
■ : DC Bias
△ : [F]
◇ : [O]
○ : [Br]
Relative [F], [O], [Br] Density
(Arb. Unit)
25
20
15
10
5
0

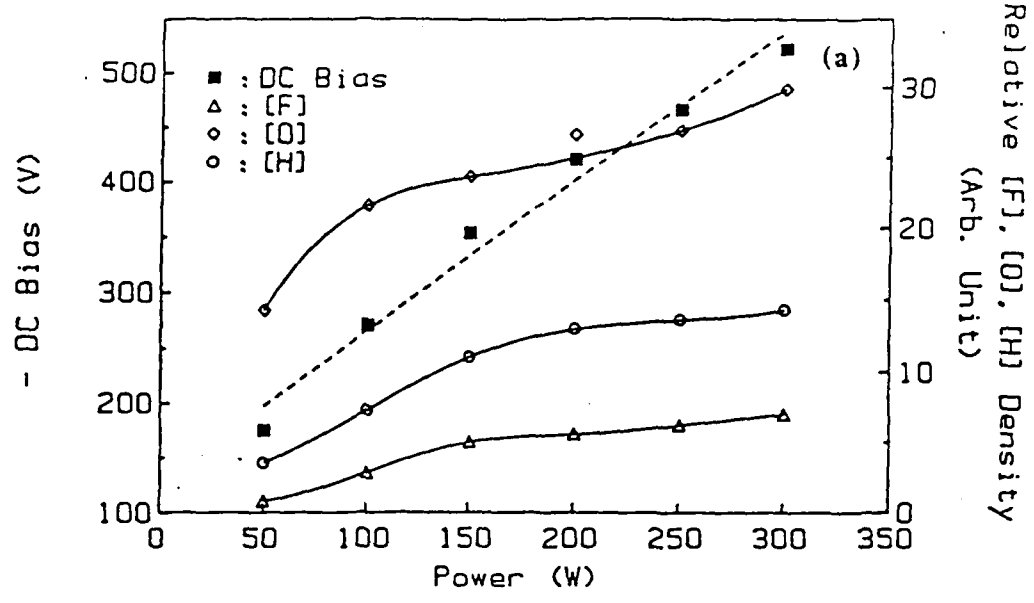

600
400
200
0
Etch Rate (A/min)
CBrF3/75%O2
(a)
■ : SiC
▲ : Si
● : SiO2
0
100
200
300
Power (W)
500
400
300
200
100
- DC Bias (V)
(b)
15
10
5
0
Relative [F], [O], [Br] Density
(Arb. Unit)
■ : DC Bias
△ : [F]
◇ : [O]
○ : [Br]
0
100
200
300
Power (W)

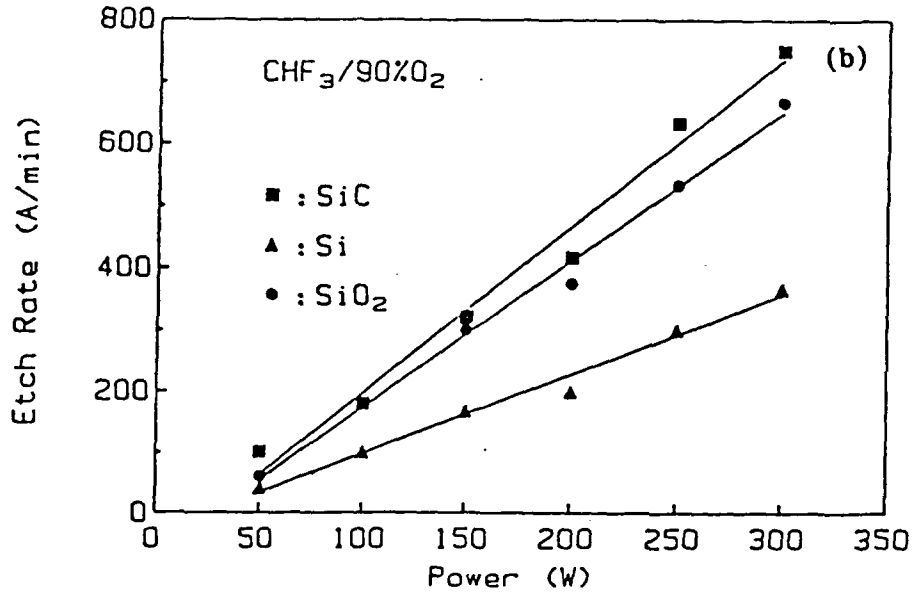

(a)
$C8rF_3/75\%O_2$
Etch Rate (A/min)
■ : SiC
▲ : Si
● : SiO_2
Pressure (mTorr)
(b)
- DC Bias (V)
Relative [F], [O], [Br] Density (Arb. Unit)
■ : DC Bias
△ : [F]
◇ : [O]
○ : [Br]
Pressure (mTorr)


(a)
CHF_3/O_2
Etch Rate (A/min)
500
400
300
200
100
0
0
20
40
60
80
100
Percentage of Oxygen (%)
■ : SiC
▲ : Si
● : SiO_2


(b)
-DC Bias (V)
500
450
400
350
300
0
20
40
60
80
100
Percentage of Oxygen (%)
30
25
20
15
10
5
0
Relative [F], [O], [H] Density
(Arb. Unit)
■ : DC Bias
△ : [F]
◇ : [O]
○ : [H]


(a)
$CHF_3/90\%O_2$
Etch Rate (A/min)
■ : SiC
▲ : Si
● : SiO_2
Pressure (mTorr)
(b)
- DC Bias (V)
Relative [F], [O], [H] Density (Arb. Unit)
■ : DC Bias
△ : [F]
◇ : [O]
○ : [H]
Pressure (mTorr)


■ : DC Bias
△ : [F]
◇ : [O]
○ : [H]
(a)
- DC Bias (V)
Relative [F], [O], [H] Density
(Arb. Unit)
Power (W)
100
200
300
400
500
0
10
20
30
0
50
100
150
200
250
300
350


$CHF_3/90\%O_2$
(b)
■ : SiC
▲ : Si
● : SiO_2
Etch Rate (A/min)
Power (W)
0
200
400
600
800
0
50
100
150
200
250
300
350

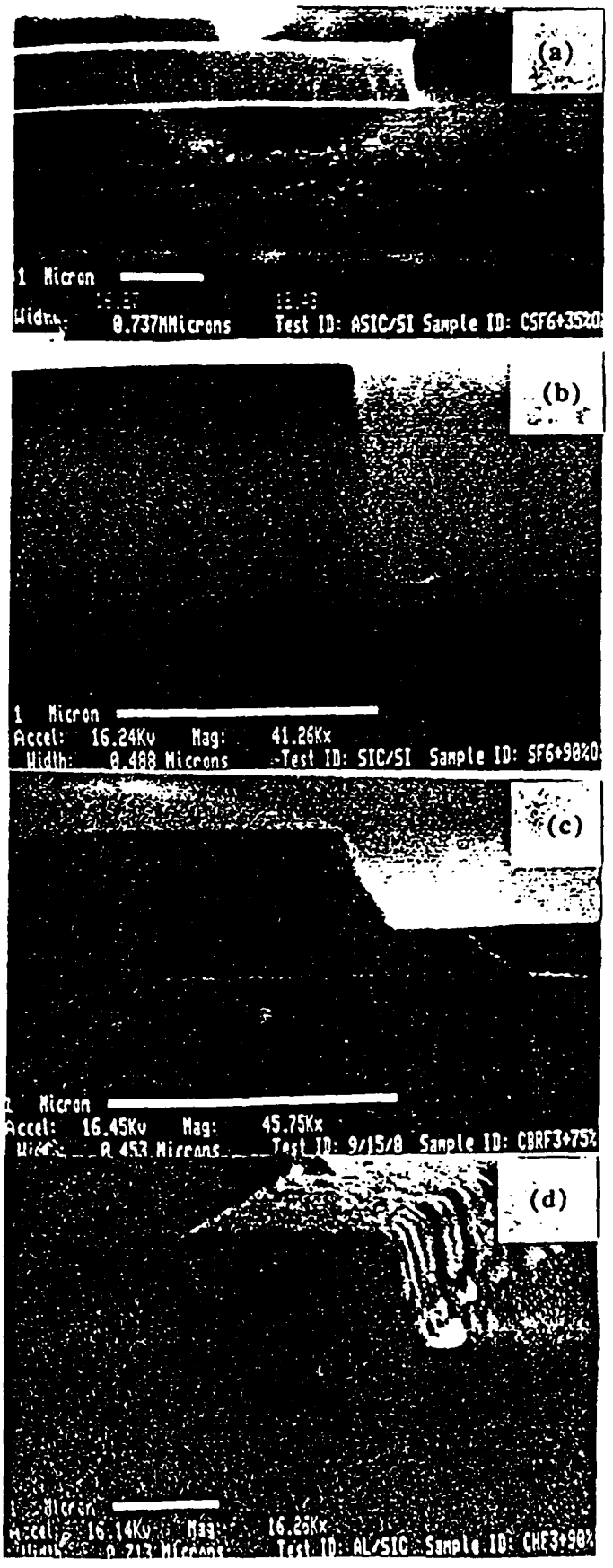
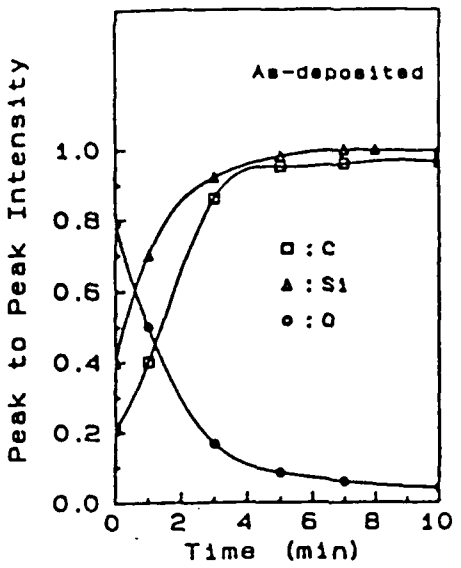
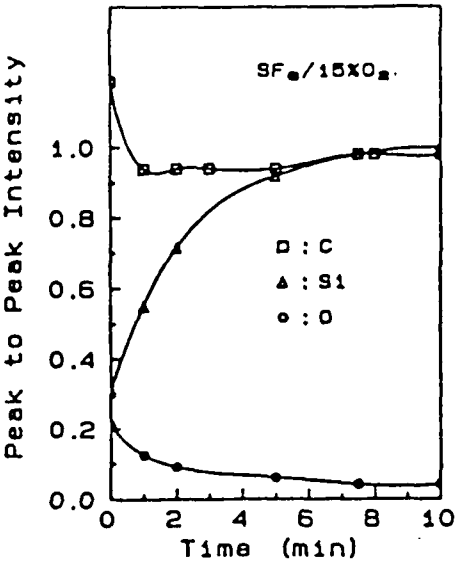
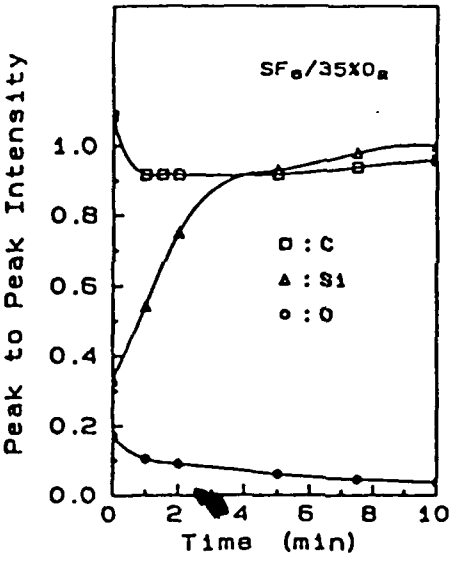
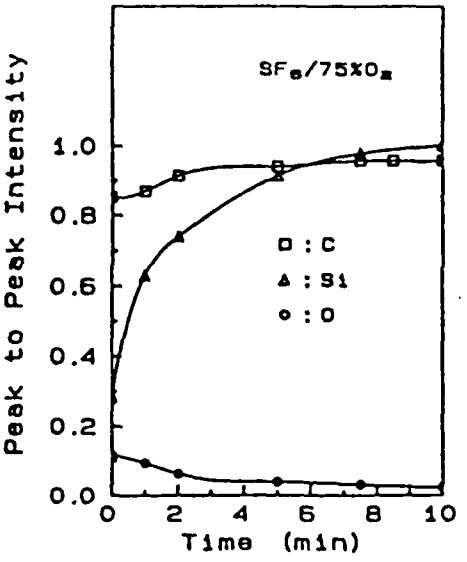


Fig. 12 Panel 5 of 6


As-deposited
Peak to Peak Intensity
Time (min)
□ : C
▲ : Si
○ : O


SF6/15%O2
Peak to Peak Intensity
Time (min)
□ : C
▲ : Si
○ : O


SF6/35%O2
Peak to Peak Intensity
Time (min)
□ : C
▲ : Si
○ : O


SF6/75%O2
Peak to Peak Intensity
Time (min)
□ : C
▲ : Si
○ : O